Preparation and Properties of the *n*-Alkyl Acrylates

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Although acrylic acid is the simplest unsaturated carboxylic acid and its ester spolymerize readily, yielding useful resins,[1a] no adequate study of the preparation and physical properties of the alkyl acrylates has been published. The commercially important methyl and ethyl esters are manufactured by treating ethylene cyanohydrin with the appropriate alcohol in the presence of sulfuric acid, a method which appears to be less suitable for production of higher alkyl acrylates.[1a] Although methyl acrylate can be made satisfactorily by pyrolysis of the acetyl derivative of methyl lactate, pyrolysis of higher *n*-alkyl α-acetoxypropionates produces low yields of *n*-alkyl acrylates.[2,3,4] Most of the published information on acrylic esters has appeared in the patent literature. The purpose of the present work was to prepare the *n*-alkyl acrylates by a generally applicable method[5] and determine their common physical properties. In addition, the esters were polymerized and examined briefly for a preliminary determination of the relation between the structure of the monomer and properties of the polymer.

The higher acrylic esters were made in the present work by alcoholysis,[6,7] a method recommended by Neher[1a] and used previously to prepare ethyl,[5] *n*-propyl,[5] *n*-butyl[5] and cetyl acrylates.[8]

Several of the *n*-alkyl methacrylates, including the *n*-propyl,[9] *n*-butyl,[7] *n*-hexyl[7,10] lauryl[11] and stearyl[11] esters, have been produced similarly by alcoholysis of methyl methacrylate. The ethyl, *n*-propyl, *n*-butyl, and dodecyl esters of acrylic acid have been prepared also by direct esterification,[12] dehalogenation of alkyl α,β-dibromopropionates with zinc,[13,14,15] dehydrohalogenation of β-halopropionic esters,[12a,16,17] acylation of the alcohol with acrylyl chloride,[8,18] dehydration of

(1) This is one of four Regional Research Laboratories operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

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(4) Lee T. Smith, C. H. Fisher, W. P. Ratchford and M. L. Fein, *Ind. Eng. Chem.*, **34**, 473 (1942).

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TABLE I

PREPARATION AND PHYSICAL PROPERTIES OF THE *n*-ALKYL ACRYLATES

Ester	Catalyst	Yield, %[a]	Alcohol converted into acrylate, %	Methyl acrylate accounted for, %[b]	Boiling point °C.	Boiling point Mm.	$n^{20}D$	d^{20}_4	Molecular refraction Calcd.[c]	Molecular refraction Found
Methyl[d]	.....	...	..	...	80	760	1.4040	0.9535	21.86	22.08
Ethyl[d]	Toluenesulfonic acid	62.7	62.7	104	43	103	.4068	.9234	26.47	26.68
Ethyl[d]	H_2SO_4	99	99	82.6	43	103	1.4068	.9234	26.47	26.68
Propyl[d]	$C_7H_7SO_3H$	100	86.6	90	44	40	1.4130	.9078	31.09	31.36
Butyl[d]	$C_7H_7SO_3H$	96	79.5	...	35	8	1.4190	.8998	35.71	36.02
Butyl[d]	$C_7H_7SO_3H$	93.4	84.4	94.2	39	10	....	....	...	...
Butyl	$Al(OBu)_3$	85.2	80.6	...	39	10	....	....	...	...
Butyl[d]	$Al(t\text{-}BuO)_3$	66	59.3	76.5	..	....	....	....	...	...
Amyl	H_2SO_4	87	87	99	48	7	1.4240	.8903	40.33	40.76
Hexyl	$C_7H_7SO_3H$	99	90	92	40	1.1	1.4285	.8882	44.95	45.30
Hexyl	H_2SO_4	99.2	95.7	88.4	89	24	1.4280	....	...	...
Heptyl	$C_7H_7SO_3H$	80.7	80.7	68.7	57	1.0	1.4311	.8846	49.57	49.91
Octyl	$C_7H_7SO_3H$	92.3	92.3	89.6	57	0.05	1.4360	.8810	54.19	54.68
Nonyl	$C_7H_7SO_3H$	91.5	91.5	100	76	0.2	1.4380	.8785	58.81	59.26
Decyl	$C_7H_7SO_3H$	96.7	83.8	88.7	120	5	1.4400	.8773	63.43	63.78
Decyl	H_2SO_4	83.5	81.9	64.3	118	5	1.4400	.8789	63.43	63.67
Dodecyl[e]	$C_7H_7SO_3H$	92	92	87	120	0.8	1.4440	.8727	72.66	73.15
Tetradecyl[f]	$C_7H_7SO_3H$	90	90	96.3	138	.4	1.4468	.8700[g]	81.89	82.30
Hexadecyl[h]	$C_7H_7SO_3H$	53.3	53.3	...	148	.04	1.4470 (30°)	.8628 (30°)[i]	91.13	81.81
Hexadecyl[h]	H_2SO_4	63	63	86.4	170	1.5	1.4460 (30°)	.8613 (30°)[j]	91.13	91.79

[a] Per cent. of theoretical on the basis of alcohol consumed. [b] Either as recovered methyl acrylate or as the higher acrylic ester. [c] From the constants recommended by Eisenlohr. [d] Data reported in a previous paper (ref. 5). [e] M. p. approximately 4°. [f] M. p. approximately 14°. [g] At 30° the density (d^{30}_4) was 0.8622. [h] M. p. approximately 24°. [i] Estimated value at 20° is 0.8706. [j] Estimated value at 20° is 0.8691.

alkyl hydracrylates,[19] or pyrolysis of alkyl α-acetoxypropionates.[2]

The alcoholysis procedure[5] used in the present investigation consisted in refluxing methyl acrylate, which can be prepared satisfactorily from either ethylene cyanohydrin[1] or lactic acid,[4] with the higher alcohol in the presence of sulfuric or toluenesulfonic acid and distilling methanol azeotropically as it was formed. This was accomplished in most of the experiments by adding an excess of methyl acrylate and removing the methanol as the methanol–methyl acrylate azeotrope, which boils at 62–63°. Petroleum hydrocarbons distilling in the approximate range of 55 to 65° also can be used to distill the methanol azeotropically.[5]

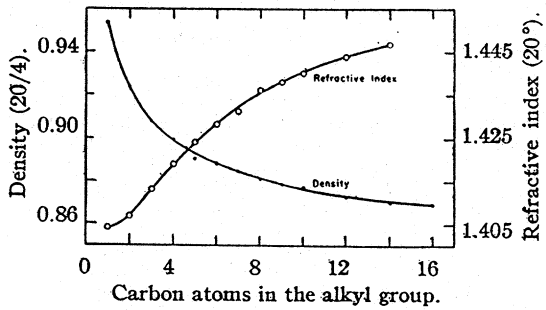

Fig. 1.—Refractive indices and densities of the monomeric *n*-alkyl acrylates.

(19) W. Bauer, U. S. Patent 1,890,277 (1932).

Our results indicate that the alcoholysis method is generally suitable for preparing acrylates of the *n*-alkanols and some of the secondary alkanols. On the basis of the alcohol placed in the reaction flask, the yields were high in most instances (Table I); on the basis of the unrecovered alcohol they were usually over 90%. Losses of methyl acrylate were low; probably these losses could be reduced in some instances by conditions which would further decrease polymerization.

When the densities and refractive indices of the *n*-alkyl acrylates were plotted against the number of carbon atoms in the alkyl group, smooth curves were obtained (Fig. 1). Figure 1 can be used to estimate the densities and refractive indices of certain *n*-alkyl acrylates not yet prepared.

A straight line having a slope of 1.185 resulted when the molecular volume at 20° of the *n*-alkyl acrylates was plotted against molecular weight. This straight line is defined by the equation molecular volume = $1.185\,M - 9.5$, where M is molecular weight.

The density (d^{20}_4) of the higher *n*-alkyl acrylates can be calculated with fair accuracy by the equation $d^{20}_4 = M/(1.185M - 9.5)$. According to Aranda,[20] straight lines having a slope of 1.167 are obtained by plotting the molecular volume of homologous series against the molecular weight.

A straight line was obtained by plotting the

(20) V. G. Aranda, *Anales soc. espan. fis. quim.*, [5] **35**, 45-63 (1940?); *C. A.*, **34**, 5329 (1940).

molecular weight of the *n*-alkyl acrylates against the molecular weight divided by the refractive index. Hence, the relation between the molecular weights and refractive indices of the *n*-alkyl acrylates are shown by the equation

$$M/n^{20}\text{D} = 0.67857M + 3.363$$

Polymeric *n*-Alkyl Acrylates.—The *n*-alkyl acrylates were emulsion polymerized, and certain properties of the polymers were determined to ascertain the effect of the length of the alkyl group on the properties of the polymer. The acrylic esters were polymerized under standard conditions to minimize differences in properties of the polymers that might be attributed to conditions of polymerization. Emulsion polymerization was used because of its convenience and the fact that polymers of relatively high molecular weight are produced by this technique. Polymers of high molecular weight were preferred because their properties should depend less on molecular weight than those of the corresponding polymers having a low molecular weight. Moreover, since many of the polymeric *n*-alkyl acrylates were known[1a] to be soft and tacky, it was anticipated that the polymers of relatively high molecular weight would be less tacky, and hence easier to handle, than the corresponding polymers of low molecular weight.

As prepared in the present work, polymethyl acrylate was tough and moderately hard, and had little or no tack at room temperature. It was flexible, extensible and somewhat rubbery. Polymerized ethyl acrylate was considerably softer and more rubber-like. The polymer of *n*-propyl acrylate was still softer and slightly tacky. The properties[1a] of the polymeric *n*-alkyl acrylates varied with the number of carbon atoms in the alkyl group, the softest and tackiest product at room temperature being tetradecyl acrylate. The polymer of *n*-hexadecyl acrylate was hard and wax-like at room temperature but soft and tacky above its brittle point (approximately 35°).

The brittle points of the polymers (Fig. 2) decreased with increase in chain length of the alkyl group for the first eight members of the series and then became progresssively higher (Fig. 2). Polymeric *n*-octyl acrylate had the lowest brittle point (−65°) of the polymers studied, and *n*-hexadecyl had the highest (+35°). The first member of the series, polymethyl acrylate, had a brittle point of +3°. According to Trommsdorff,[21] the polymers of methyl, ethyl and *n*-butyl acrylates have brittle points of +8, −20 and −40°, respectively. The curve in Fig. 2 indicates that the acrylates obtained from the normal alcohols of twenty-four or more carbon atoms would yield wax-like polymers with comparatively high softening points.

The solubility behavior of the polymeric *n*-alkyl acrylates in acetone, ethyl acetate, toluene and heptane was studied briefly. Acetone and ethyl acetate dissolved the resins prepared from the lower acrylic esters (up to about hexyl acrylate) but had little effect on the polymers of the higher esters. Toluene dissolved the lower acrylates (up to those having twelve to fourteen carbon atoms in the alkyl group (and caused the higher ones to swell and disintegrate. Heptane swelled the lower acrylates, dissolved those of intermediate chain length, and swelled and disintegrated the higher acrylates.

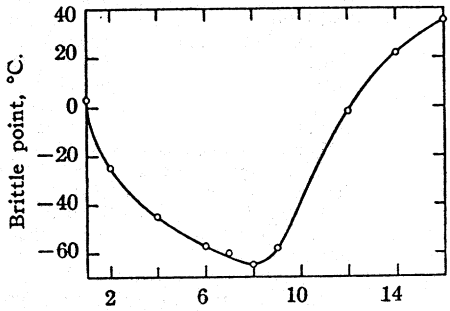

Fig. 2.—Brittle temperatures of the polymeric *n*-alkyl acrylates.

Experimental

Alcoholysis of Methyl Acrylate.—In most of the experiments three or four times the theoretical quantity of methyl acrylate was used, and the methanol–methyl acrylate azeotrope was distilled during the alcoholysis. Sulfuric acid, *p*-toluenesulfonic acid, or aluminum alcoholate was used as catalyst, the first being preferred. Hydroquinone or *p*-phenylenediamine (3 to 5% by weight of the methyl acrylate) was used to inhibit polymerization. The mixture of methyl acrylate, the higher alcohol, hydroquinone, and sulfuric acid was heated (oil-bath) in a flask attached to a fractionating column that supported a total-condensation partial take-off distilling head. The system was operated under total reflux until the methanol–methyl acrylate azeotrope began to collect at the stillhead. The take-off was then adjusted so that the azeotrope was removed as it was formed. When formation of the azeotrope ceased, the mixture was fractionally distilled. Although diminished pressure decreased the likelihood of polymerization, the lower acrylic esters could be distilled under atmospheric pressure.

With 2 moles of primary alcohol, 6 moles of methyl acrylate, 1 ml. of sulfuric acid, and 10 to 15 g. of hydroquinone, the reaction usually required six to ten hours, although most of it occurred in the first two to four hours. One advantage of attaining practically complete reaction is that the necessity of separating unreacted alcohol from the corresponding acrylate is avoided. This separation sometimes offers some difficulty in fractionation, since the acrylates usually have boiling points only 15 to 30° above those of the corresponding alcohols.

The relatively low yields of acrylic ester and high losses of methyl acrylate observed in some of the experiments generally were caused by losses suffered through partial polymerization of the esters. In some of the earlier experiments the amount of inhibitor used was only 1 to 2% of the amount of the acrylate, and some polymer was formed in the reaction flask. Use of from 3 to 5% of inhibitor, and an oil-bath for heating, eliminated this loss in later experiments. Occasionally some polymer formed in the fractionating column, stillhead, or receiver, but exclusion of air and passing a slow stream of carbon dioxide through the still eliminated most of this trouble.

Aluminum alcoholate was used as catalyst in two experiments. In the first, amalgamated aluminum foil was dissolved in butanol. In the second, a commercial sample of

(21) E. Trommsdorff, *Kunststoffe*, **27**, 75–79 (1937).

aluminum *t*-butoxide was used. The decreased yields obtained with the aluminum catalyst were due partly to formation of polymer, whereas the lower conversions were due to a slower reaction than that obtained with sulfuric acid as catalyst.

Glass Vigreux columns and columns packed with nickel gauze (Lecky–Ewell) or copper were used for the distillations. The inhibiting effect of copper was doubtful, since polymerization occurred in some instances with copper-packed columns. The principal factors involved in preventing polymerization in the distillation column appeared to be (1) rigid exclusion of air and (2) use of columns of low holdup. Introduction of a slow stream of carbon dioxide during the reaction and distillation helps to exclude air. All joints and connections should be airtight, and the entire system should be closed to the atmosphere or filled with oxygen-free carbon dioxide if it becomes necessary to interrupt the reaction or distillation and allow the system to cool. In connection with the liquid holdup in the column, bubble-cap and certain packed columns appear less suitable than the Vigreux, Lecky–Ewell and spiral-packed columns. The difficulty of removing the polymer after it has formed in the column, as well as the prevention of polymerization, merits consideration in the selection of a distillation column.

Methyl acrylate can be recovered from its methanol azeotrope, which contains approximately 54% of alcohol and 46% of ester, by washing out the methanol with water (preferably brine) or by adding a third component that will form a suitable low-boiling binary azeotrope with either the methanol or methyl acrylate and distilling. A petroleum fraction boiling within a range of 2 or 3°, preferably between 50 and 65°, is satisfactory for removing methanol both from the reaction mixture during the alcoholysis and from the methanol–methyl acrylate azeotrope. For the former purpose, the requirements are rigid. Since the entraining agent should be easily removed from the reaction mixture after all the methanol has been distilled, the boiling point of the entraining agent should not be higher than approximately 65°, and should not be below approximately 50°, because the alcoholysis would be too slow at the lower temperatures. It should not distill azeotropically with the acrylic esters. With methanol it should form a binary azeotrope that boils at a temperature considerably below the distilling temperature (62 to 63°) of the methanol–methyl acrylate azeotrope. Finally, it should be easy to separate the entraining agent from the methanol in the distillate, preferably by virtue of insolubility. All these requirements are met satisfactorily by a petroleum fraction boiling at 59 to 61°, and this fraction has been used successfully in the present work to remove methanol continuously during alcoholysis and to separate methanol from the methanol–methyl acrylate azeotropic distillate.

The methanol–hydrocarbon azeotrope boils at 47 to 48° and contains approximately 18% methanol. It separates into two layers, the ratio and composition of which depend upon the temperature. At about 20° the ratio of the methanol (lower) layer to the petroleum ether (upper) layer is about 1:4, and there is about 8.8% methanol in the upper layer and 60% in the lower. More complete separation can be effected by cooling the mixture.

Acrylic Ester Azeotropes.—Preparation of ethyl, *n*-propyl and isopropyl acrylates from methyl acrylate by alcoholysis is complicated by the fact that the corresponding alcohols form binary azeotropes with methyl acrylate. Moreover, ethyl acrylate forms binary azeotropes with both methanol and ethanol. The approximate compositions and boiling points of these azeotropes are shown in Table II. Apparently, methyl acrylate does not form an azeotrope with *n*-butanol, *i*-butanol or ethyl acrylate. In addition to the azeotropes described in Table II, methyl acrylate forms an azeotrope with water that boils at 71° and consists of approximately 7.2% water and 92.8% methyl acrylate. This mixture separates into two layers, about 93.7% being in the upper layer and 6.3% in the lower. The upper layer contains about 1.5% water and 98.5% methyl acrylate; the lower contains 6.7% ester and 93.3% water.

TABLE II

PROPERTIES OF ALCOHOL–ACRYLIC ESTER AZEOTROPES

Acrylic ester	Alcohol	Boiling point of azeotrope, °C.	Composition of azeotrope, %[a] Acrylic ester	Alcohol
Methyl	Methyl	62.5	46.0	54.0
Methyl	Ethyl	73.5	57.6	42.4
Methyl	*n*-Propyl	79.0	94.6	5.4
Methyl	*i*-Propyl	76.0	53.5	46.5
Ethyl	Methyl	64.5	15.6	84.4
Ethyl	Ethyl	77.5	27.3	72.7

[a] Estimated from refractive indices. By determining the refractive indices of syntheic mixtures it was shown that this method is satisfactory.

In the preparation of ethyl acrylate from the methyl ester by alcoholysis, methanol, ethanol, methyl acrylate and ethyl acrylate are present in the reaction mixture. Each alcohol forms a binary azeotrope with each acrylate, and therefore the mixture contains components boiling at 62.5, 64.5, 64.7, 73.5, 77.5, 78.4, 80 and 100°, even if the possibility of ternary, or higher, azeotropic mixtures is excluded. On first consideration, the separation of such a mixture by distillation would appear nearly impossible, but high yields of ethyl acrylate were readily obtained, as described below.

The reaction mixture was heated initially under total reflux for several hours until the concentration of methanol was increased and that of ethanol decreased so far that the methanol–methyl acrylate azeotrope could be distilled without appreciable loss of ethanol. The methanol–methyl acrylate azeotrope was then allowed to distill slowly, the vapor temperature at the stillhead never being allowed to exceed 63°. After all the ethanol had been consumed and all the methanol had been removed, the distillation became only a matter of separating methyl and ethyl acrylates.

Polymerization.—The monomeric esters were polymerized by heating at about 90° (with mechanical stirring) a mixture of 50 g. of acrylic ester, 100 g. of water, 0.5 g. of Triton K60 (cetyldimethylbenzylammonium chloride),[22] and small quantities of hydrogen peroxide (27.5 or 30%) or of a mixture of hydrogen peroxide and benzoyl peroxide. In most experiments, hydrogen peroxide was added in small quantities until polymerization started. In the few instances when this procedure seemed ineffective, treatment with hydrogen peroxide was followed by the addition of a small amount of benzoyl peroxide.

Coagulation sometimes occurred spontaneously after the polymerization or as the result of the agitation and changes in temperature. The polymers were coagulated from the more stable emulsions by the addition of an aqueous solution containing acetic acid and calcium chloride, washed with distilled water, and dried. The air-dried polymers were then heated for twelve to twenty hours at about 80°. The solubility behavior of the polymers was ascertained by allowing approximately 0.5 g. of the sample to stand in contact with 10 ml. of solvent for at least two days. The behavior of the polymers at low temperatures was determined by bending with tongs samples immersed in a cooled ethanol-bath. The temperature at which the specimens broke was considered the brittle point. The temperature of the bath was regulated by adding solid carbon dioxide. High precision cannot be claimed for results obtained in this manner, but polymers that were soft and tacky at room temperature could not be handled conveniently in any other way, and the data obtained do indicate the approximate brittle temperatures.

The polymerizations appeared to be virtually complete, and it is believed that only negligible amounts of monomeric acrylic esters remained in the oven-dried polymers. Monomeric esters would be expected to soften the polymers, lower the brittle point, and increase tackiness. On

(22) F. J. Van Antwerpen, *Ind. Eng. Chem.*, **35**, 126–130 (1943).

the basis of two experiments in which the polymerization yield was carefully determined, and because our brittle points agreed with those of Trommsdorff,[21] it is believed that the properties of our polymers were not greatly influenced by monomeric esters.

Summary

Higher *n*-alkyl acrylates having two to sixteen carbon atoms in the alkyl group were prepared in high yields by the alcoholysis of methyl acrylate. The monomeric esters were emulsion polymerized, and the coagulated polymers were examined briefly to determine the influence of chain length of the alkyl group upon the properties of the polymer. As the chain length of the alkyl group increased, the polymers became softer and tackier at room temperature (up to and including tetradecyl acrylate). The polymer of *n*-hexadecyl acrylate was a wax-like solid at room temperature but soft and tacky above 35°. As the molecular weights increased, the brittle points of the first eight polyalkyl acrylates became lower; beyond octyl acrylate, which had a brittle point of −65°, the brittle points became higher.